Isotope Dilution Mass Spectrometry of Nickel in Some Ultra Pure Reagents and Seawater

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Abstract

Isotope dilution surface ionization mass spectrometry has been successfully applied to the accurate determination of nickel in ultra pure acids and ammonia prepared by subboiling analytical grade reagents, and also in pure water and seawater. After spiked with a stable isotope of nickel ${}^{61}Ni$, the sample is heated to dryness and the residue obtained is dissolved in a mixture of a phosphoric acid and silica gel suspension aqueous solution. An aliquot of this solution is applied to the mass spectrometer equipped with a surface ionization device incorporating a rhenium single filament. By measuring the ${}^{58}Ni/{}^{61}Ni$ ratio, the present method can determine ng amount of nickel with a relative error of 1%, the detection limit being 10^{-13} g.

1 Introduction

When nickel in a weighed amount of samples has reached isotopic equilibration whit a known amount of a ${}^{61}Ni$ enriched spike, a following relation holds for the molar amounts of the element and its isotopes;

$$ {}^{58}\mathrm{Ni} \big/ {}^{61}\mathrm{Ni} = \frac{{}^{58}f\mathrm{Ni{-}sample} \ \mathrm{x}\ X + {}^{58}f\mathrm{Ni{-}spike}\ \mathrm{x}\ Y}{{}^{61}f\mathrm{Ni{-}sample}\ \mathrm{x}\ X + {}^{61}f\mathrm{Ni{-}spike}\ \mathrm{x}\ Y} \qquad (1) $$

where ${}^{58}Ni$ and ${}^{61}Ni$ represent the molar amounts of isotope ${}^{58}Ni$ and ${}^{61}Ni$ comprising nickel under measurement; X and Y are the molar amounts of the element in the sample and the added spike; and ${}^{58}f$Ni-sample and ${}^{61}f$Ni-spike are the isotopic abundances of the isotope ${}^{58}Ni$ in the sample and ${}^{61}Ni$ in the spike respectively. The amount of X can be determined by measuring the ${}^{58}Ni/{}^{61}Ni$ ratio, when the amount of Y is known.

When a certain amount of Y is added to a sample, the resulting ${}^{58}Ni/{}^{61}Ni$ ratio moves along the isotope dilution curve according to the amount of X as shown in Fig. 1. Different amounts of Y will make corresponding curves parallel to that in Fig. 1. Sample preparations must be carefully performed to make the ${}^{58}Ni/{}^{61}Ni$ ratio fall on close to the Z point in Fig. 1, where the most accurate value of X is obtained [1]. The lack of purity in the isotopic abundance of the ${}^{61}Ni$ spike makes the tangent value of this isotope dilution curve smaller than those of cadmium, lead, silver, thallium, etc. This means that unsuitable ${}^{58}Ni/{}^{61}Ni$ ratios will give large error to the analytical results of nickel.

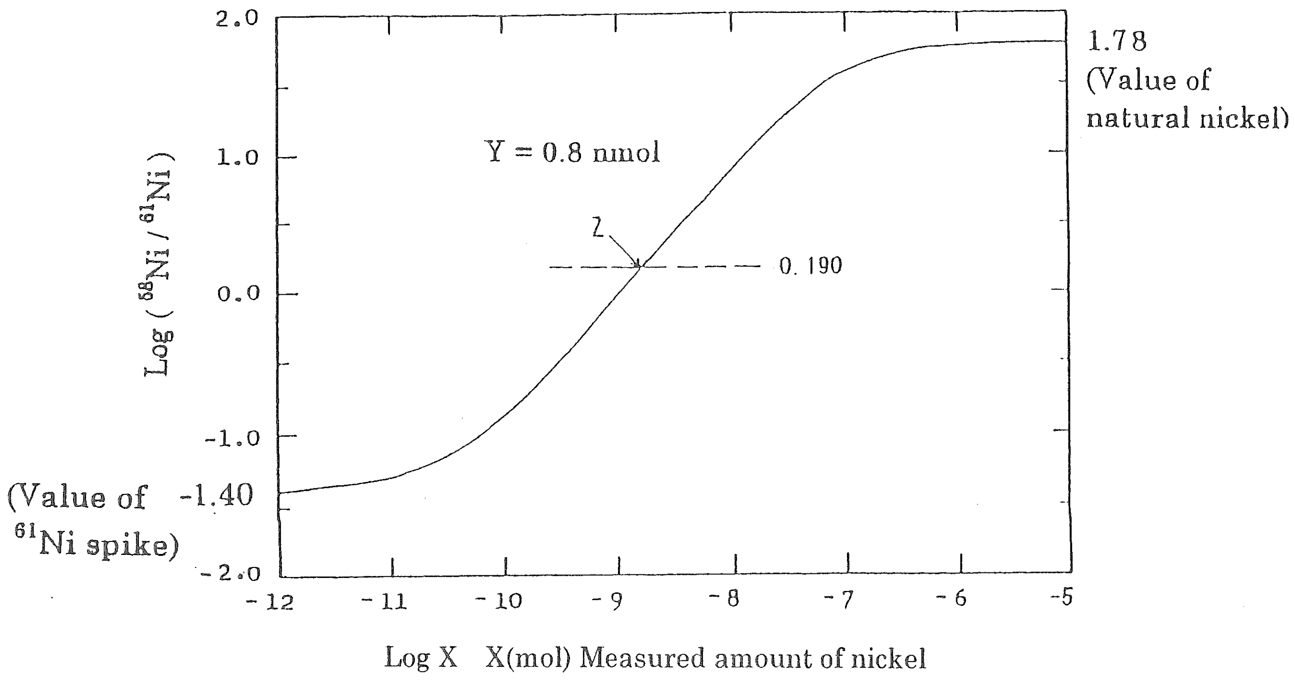

Fig. .1 Isotope dilution curve X(mol) Measured amount of nickel

2 Experiments

^{61}Ni spike solution

A weighed amount of the ^{61}Ni enriched nickel metal was dissolved in a dilute nitric acid solution and stored in a tightly stoppered teflon bottle. The isotopic abundance of this nickel was determined and listed together with that of a commercial Four-9 nickel metal and that of the certified value by the Oak Ridge National Laboratory, Tenn., U. S. A. in Table 1.

The molar concentration of this spike solution was standardized to a reference nickel solution, which had been prepared from the Four-9 metal, and is shown in Table 2.

Mass spectrometer

A Hitachi RMU-6 mass spectrometer detected an emitter current of 10^{-19}A for the Ni^{+} mass spectrum and measures the isotopic ration with an accuracy of 0.n % in the coefficient of variation.

Reagents and laboratory

All chemical procedures were performed in a class 100 clean draft chamber and on class 100 clean benches set in a class 300 clean room.

Sample preparation for mass spectrometry of nickel in ultra pure reagents

A weighed amount of ^{61}Ni spike solution, usually 0.8 nmol as ^{61}Ni was added to the addition of nitric acid, each 5 nmol of ^{61}Ni spike was added as indicated in Table 4. After setting stood for several days to reach the isotopic equilibrium, the spike sample was neutralized to a pH value of 9. Nickel was extracted into 10 ml of a 0.0013% dithizone chloroform solution. Then, the solution was rinsed several times with each 5.0 ml of purified water to remove the aqueous emulsion containing the major components of seawater. A 5.0 ml portion of 7 mol kg^{-1} nitric acid was added to the dithizone chloroform solution for the back extraction of the element. The acid solution was rinsed twice with 5.0 ml portions of chloroform solution. The acid solution was transferred to a teflon beaker and 1.0 ml of nitric acid and 0.25 ml of perchloric acid were added. The contents were gently heated to dryness under a pure nitrogen atmosphere in an oven. Subsequently, 0.3 ml of nitric acid and 0.1 ml of perchloric acid were added to the residue and the contents were heated again to decompose completely the organic materials. The residue thus obtained was dissolved in the above mentioned mixture solution.

3 Discussion and Conclusion

Emission of Ni$^+$ ion beam current

As shown in Table 1, the use of silica gel and phosphoric acid permits 0.50 nmol of nickel to emit 1.5 x 10^{-14} A of ^{61}Ni$^+$ beam current for a long time and sometimes 0.025 nmol of nickel to do 10^{-15}A of ^{61}Ni$^+$. The mass spectrometer can catch 10^{-19} A of ion beam current due to Ni$^+$ mass spectrum, so the present method detects the presence of 10^{-13} – 10^{-12} g of nickel on the ionization filament. As Y in Eqn. (1) 0.8 nmol of the spike is enough for the present method.

Isotopic abundance of natural and spike nickel

The isotopic abundance measured by loading 11.0 nmol were used as substitute for ^{58}fNi-spike and ^{61}fNi in Eqn. (1). They are in good accordance with those determined by the Oak Ridge National Laboratory, within the analytical error. However, measured isotopic abundance of the ^{61}Ni spike has a certain variation with decreasing amount of loaded spike as shown in table 1. The lesser the loaded amount, the smaller the isotopic abundance of ^{61}Ni. This tendency tells us that the present method suffers contaminations amounting to 0.06± 0.02 ng of nickel from laboratory environments. For ^{58}fNi and ^{61}Ni, 68.3 and 1.12 are substituted.

Determination of nickel in reagents

The data in Table 3 show the applicability of the present method to the determination of nickel at the level of ng.kg^{-1} concentration with an error of 1%, samples taken being lesser than 10^2 g. Subboiling distillation effectively works to decrease nickel contaminant from the 0.1 ppb level in commercial reagents to one third of that in purified ones.

Application to seawater samples

Dithizone chloroform extraction was used to develop the present method to the simultaneous determination method for silver, cadmium, copper, nickel, lead, zinc and thallium in seawater1). A sample solution as shown in Table 3. The spiked solution was heated to dryness under a nitrogen atmosphere in a teflon oven. The residue was dissolved in a mixture solution of 65 μl of 0.2% silica gel suspension aqueous solution and 5 μl of 2.0% phosphoric acid solution for the mass spectrometry.

Table 1 Determination of isotopic abundance of natural nickel and ^{61}Ni-enriched spike.

Sample taken nmol	^{58}Ni^{+} emitted (10^{-14} A)	Isotopic abundance (%)				
Natural Ni as ^{58}Ni		^{58}Ni	^{60}Ni	^{61}Ni	^{62}Ni	^{64}Ni
13.4	2.30	68.3	26.2	1.12	3.55	0.88
3.15	5.90	68.3	26.1	1.12	3.56	0.88
0.580	0.85	68.4	26.1	1.12	3.53	0.89
0.123	0.17	68.4	26.1	1.13	3.53	0.89
0.062	0.16	68.4	26.0	1.12	3.55	0.90
^{61}Ni spike as ^{61}Ni	^{61}Ni^{+} emitted					
11.0	2.5	3.51	6.12	88.9	1.40	0.12
5.14	1.2	3.52	6.11	88.9	1.39	0.13
3.19	2.0	3.54	6.12	88.8	1.39	0.12
0.50	1.5	3.64	6.15	88.7	1.40	0.12
0.10	0.2	4.01	6.27	88.2	1.41	0.12
0.060	0.1	4.33	6.36	87.8	1.42	0.12
Certified value by ORNL		3.45	6.12	88.8	1.10	0.20

Table 2 Standardization of a ^{61}Ni spike solution to a standard solution prepared from four-9 natural metal

^{61}Ni spike solution taken, g	Natural nickel added μ mol	^{61}Ni^{+} emitted (10^{-14}A)	^{58}Ni/^{61}Ni	Spike nickel found	
				μ mol	μ mol/g
0.7020	0.7002	0.6	0.5520 (0.2)a)	1.037	1.478
0.7465	2.517	1.5	1.739 (0.1)	1.103	1.477
0.7831	2.584	1.0	1.704 (0.1)	1.156	1.476
0.7515	6.237	1.3	4.06 (0.1)	1.090	1.477
				Ave	1.477

a) Coefficient of variation (%)

Sample preparation for mass spectrometry of nickel in seawater samples

To four aliquots of a seawater sample which had been kept at a pH value of 1 by sample preparations requires the use of several reagents and apparatus from which samples suffer contamination as listed in Table 4, i.e., 1.4 ng of nickel for seawater analysis. Amount of contaminant corresponds to 1% of measured values.

Table 3 Determination of nickel in reagents, water and seawater

Sample		Sample taken (g)	Spike added as total spike nmol	^{58}Ni/^{61}Ni	C.V.$^{a)}$ (%)	Nickel found in sample	
						p mol	ng kg^{-1}
A	HNO_3	45.15	0.7614	0.156	0.2	117	152
	$HClO_4$	31.01	0.7543	0.134	0.5	93.8	177
	HF	45.40	0.7601	0.143	0.4	103	133
	$CHCl_3$	71.92	0.7607	0.0583	0.7	18.5	15.2
	NH_3aq	42.25	0.7857	0.140	0.2	104	144
B	HNO_3	45.07	0.7779	0.0628	0.4	23.7	30.9
	$HClO_4$	74.70	0.7827	0.0770	0.3	37.0	29.1
	HF	48.60	0.8256	0.0647	0.6	27.1	32.8
	$CHCl_3$	83.97	0.7820	0.0490	0.5	9.36	6.54
	NH_3aq	50.56	0.7827	0.0742	0.5	34.3	39.7
	water	706.1	0.7909	0.102	0.5	62.4	5.18
Seawater		623.2	5.063	0.654	0.2	4.11×10^3	385
		620.6	5.032	0.652	0.2	4.03×10^3	383
		1239.5	5.203	1.208	0.1	8.09×10^3	382
		1240.3	5.109	1.227	0.1	8.08×10^3	381

A: Ultra pure grade, B: Purified by subboiling distillation, a): Coefficient of variation.

Table 4 Blank for a sample preparation, ng per analysis

Sample	Reagent used	(g)	Nickel contamination from reagent ng
Seawater	HNO_3	9.6	0.4
	NH_3aq.	10.0	0.4
	$HClO_4$	0.4	0.01
	$CHCl_3$	45.0	0.3
	water	33.0	0.2
	room environments		0.06
		Total	1.4

The isotope dilution mass spectrometry of nickel has following inherent advantages. All chemical manipulations are done on a weight basis and involve straight-forward stoichiometric separations to determine amounts of nickel in samples and the ^{61}Ni spike solution, and the mass spectrometric determinations involve only ratios but not absolute determinations of the isotopes. Furthermore, instrumental sensitivity and accuracy are essentially high, no instrumental corrections being necessary. Thus, the present method can detect 10^{-12} - 10^{-13} g of nickel and measure pmol level of nickel with a relative error of 1%.

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Keywords

Isotope dilution mass spectrometry; nickel in ultra pure reagent

nickel in ultra pure water; nickel.